

TECHNICAL ARTICLE

Clinoptilolite Zeolite Influence on Inorganic Nitrogen in Silt Loam and Sandy Agricultural Soils

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Abstract: Development of best management practices can help improve inorganic nitrogen (N) availability to plants and reduce nitrate-nitrogen ($\text{NO}_3\text{-N}$) leaching in soils. This study was conducted to determine the influence of the zeolite mineral clinoptilolite (CL) additions on $\text{NO}_3\text{-N}$ and ammonium-nitrogen ($\text{NH}_4\text{-N}$) in two common Pacific Northwest soils. The effects of CL application rate (up to 26.9 Mg ha^{-1}) either band applied or mixed with a set rate of N fertilizer on masses of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in leachate and soil were investigated in a column study using a Portneuf silt loam (coarse-silty mixed mesic Durixerollic Calciorthid) and a Wolverine sand (Mixed, frigid Xeric Torripsamment). All treatments for each soil received a uniform application of N from urea fertilizer, with fertilizer banded or mixed with CL. In the Portneuf soil, band application of CL and N contained 109% more total inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) in the soil/leachate system compared with mixing. In both soils, CL application rate influenced the quantity of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the leachate and soil. Application of CL at rates of 6.7 to 13.4 Mg ha^{-1} resulted in the conservation of inorganic N in the soils. Band applying CL and N seems to conserve available inorganic N in the soil compared with mixing CL and N possibly because of decreased rates of microbial immobilization, nitrification, and denitrification.

Key words: Zeolite, clinoptilolite, nitrogen, ammonium, nitrate.

(*Soil Sci* 2010;175: 357–362)

Nitrogen (N) from fertilizers is needed to optimize and sustain crop production in agronomic systems but is susceptible to leaching and denitrification loss from soils. Nitrogen losses caused by leaching and denitrification from agricultural land, especially in sandy soils, are an environmental and economic concern (Perrin et al., 1998). Nitrogen loss from irrigated cropland can significantly contribute to nitrate levels in surface water and groundwater and can subsequently lead to waterway impairment and eutrophication. On a national scale, agriculture accounts for 50% and 60% of impaired lakes and rivers, respectively (US EPA, 2006). Thus, preventing off-site nutrient movement is of paramount importance.

A means of lessening off-site N movement into waters, and in particular N from land-applied N fertilizer, is by application timing and placing N fertilizers in bands below the soil surface. For example, band application of urea-N and anhydrous $\text{NH}_3\text{-N}$ in moist soil will result in less $\text{NH}_3\text{-N}$ volatilization losses compared with surface applications because of the ability of moist soils to retain ammonium-nitrogen ($\text{NH}_4\text{-N}$) and a greater distance before it reaches the atmosphere at the soil surface (Bouwmeester et al., 1985; Tisdale et al., 1985). Band applica-

tion of N fertilizers also removes it from surface runoff pathways. Williams et al. (2003) broadcast or band applied 350 kg of urea-N ha^{-1} approximately 3 weeks after sowing spinach (*Spinacea oleracea* L.), followed by a 50-kg N ha^{-1} (again broadcast or band) 4 weeks later. The authors noted that N leaching losses were greater with the broadcast fertilizer treatment (246 kg N ha^{-1} lost) as compared with banded (186 kg N ha^{-1} lost). Prasertsak et al. (2002) either surface applied or drilled N-labeled urea 3 to 4 days after sugarcane (*Saccharum officinarum* L.) harvest. Although banding increased denitrification and leaching losses as compared with surface application, the total N loss was reduced from 59.1% to 45.6% with drilling as compared with surface application, resulting in an extra 10% of applied N assimilated in the crop. These management practices have been studied and introduced to directly or indirectly reduce N leaching in many agricultural systems. However, other new technologies associated with soil conditioners, such as zeolite minerals, have the potential to further reduce soil N leaching losses.

Zeolites are naturally occurring aluminosilicate minerals (Kithome et al., 1998). More than 50 different types of zeolite minerals have been found (Tsitsishvili et al., 1992). They are composed of tectosilicates with isomorphous substitution of Al^{+3} and Si^{+4} and have high cation exchange capacities (CEC) (Perrin et al., 1998) because the clinoptilolite (CL) framework structure consists of interlinked four and five tetrahedral rings that create a layer; between these layers are 8 and 10 open tetrahedral ring channels (Vaughan, 1978). This open structure leads to increased CL surface area and has been measured at $9.25 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$ (Kithome et al., 1998). Consequently, increased surface area produces a material with increased CEC. The theoretical CEC of the zeolite mineral CL is $220 \text{ cmolc kg}^{-1}$ (Ming and Mumpton, 1989). Furthermore, the structure of CL makes the mineral highly selective for K^+ and NH_4^+ and less selective for Na^+ and divalent cations such as Ca^{+2} (Perrin et al., 1998). Theoretically, the affinity of CL for NH_4^+ along with CL open mineral structure can potentially protect NH_4^+ from microbial access and thus reduce nitrification rates.

A number of research projects have shown increased growth and/or yield of a variety of crops caused by either an effect of zeolites on improved N use efficiency or reduced NH_4^+ toxicity (Huang and Petrovic, 1994; Minato, 1968; Torri, 1978; Moore et al., 1982; Stoilov and Popov, 1982). Research evaluating the effect of CL on $\text{NH}_4\text{-N}$ and nitrate-nitrogen ($\text{NO}_3\text{-N}$) leaching through soil has also been reported. MacKown and Tucker (1985) found that mixing CL into a loamy sand at rates of 50, 105, or 210 Mg ha^{-1} , with a constant rate of ammonium sulfate applied at $440 \text{ kg NH}_4\text{-N ha}^{-1}$, reduced $\text{NH}_4\text{-N}$ leaching through columns compared with a control. Nitrate-N was not measured because of the addition of a nitrification inhibitor with the N source. However, Huang and Petrovic (1994) found that mixing CL into simulated sand-based golf course greens at a rate equal to 10% of the soil mass (414 Mg ha^{-1}) reduced $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ leaching through lysimeters compared with a control. The purpose of the present study was

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Received February 9, 2010.

Accepted for publication May 11, 2010.

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ISSN: 0038-075X

DOI: 10.1097/SS.0b013e3181e771d1

to determine $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ leaching potential through common agricultural soils in the Pacific Northwest United States amended with an agronomic rate of N fertilizer and various rates of CL obtained from a local source.

MATERIALS AND METHODS

Soils

A Portneuf silt loam (coarse-silty mixed mesic Durixerollic Calciorthid) was collected from a depth of 0 to 30 cm in an agricultural field at the USDA-ARS Northwest Irrigation and Soils Research Laboratory in Kimberly, ID. A Wolverine sand (Mixed, frigid Xeric Torripsamment) was collected from a depth of 0 to 30 cm in an agricultural field near Firth, ID. Both soils are found in row crop production areas. The Portneuf soil is primarily found in southern Idaho and occupies approximately 117,000 ha (NRCS, 2009a). The Wolverine soil is primarily in southern Idaho and Oregon and occupies approximately 11,000 ha (NRCS, 2009a). Although the Wolverine soil does not occupy as large of an area as the Portneuf soil, soils similar to the Wolverine series (Xeric Torripasamment soils) occupy more than 5 million ha from the western United States to the Great Plains (NRCS, 2009a). After collection, the soils were air-dried and passed through a 5-mm sieve before analysis. Soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations were determined using the method of Mulvaney (1996). The Portneuf soil contained 25.2 kg $\text{NO}_3\text{-N}$ ha⁻¹ and 7.9 kg $\text{NH}_4\text{-N}$ ha⁻¹. The CEC of the Portneuf soil in the surface 4 cm ranges from 9.7 to 17 cmol(+) kg⁻¹ (NRCS, 2009b). The Wolverine soil contained 10.5 kg $\text{NO}_3\text{-N}$ ha⁻¹ and 1.1 kg $\text{NH}_4\text{-N}$ ha⁻¹. The CEC of the Wolverine soil in the surface 2.4 cm ranges from 4 to 7 cmol(+) kg⁻¹ (NRCS, 2009b).

Column Study

This study was separately conducted for each soil, with 32 soil columns for the Portneuf soil and 40 columns for the Wolverine soil used. Each column was constructed from polyvinyl chloride with a diameter of 10.6 cm and a height of 31 cm. Each column had nylon mesh glued to the bottom with a 10.6-cm-diameter ring of filter paper. For the Portneuf soil, a 2.5-cm layer of acid (1 M HCl) washed sand (475 g) was added above the nylon mesh and filter paper to retain soil in columns and filter soil particles from leachate. For the Wolverine soil, no sand was added to the bottom of the columns because of the coarse texture of the Wolverine soil. For each soil, half of the total soil (1.5 kg) was added to each column.

Clinoptilolite was obtained from the Zeocorp LLC-owned mine located in Hines, OR. The properties of the CL are found in Table 1. Treatments for the Portneuf soil consisted of four CL rates (0, 6.7, 13.4, and 20.1 Mg ha⁻¹) and two application methods of CL and N fertilizer (mixed and band). Treatments for the Wolverine soil consisted of five CL rates (0, 6.7, 13.4, 20.2, and 26.9 Mg ha⁻¹) and the two CL/N application methods. For each soil type, all CL rate treatments received an N fertilizer application rate of 224 kg N ha⁻¹ as urea (46% N) on an area basis. The N fertilizer application rate was based on University of Idaho N fertilizer recommendations for Russet Burbank potatoes. The quantity of $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$ added to each soil with the CL was small compared with the N added in urea. The $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$ applied in the CL to the Portneuf soil represented from 0.03% to 0.08% of the N applied in urea and CL. The $\text{NO}_3\text{-N}$ plus $\text{NH}_4\text{-N}$ applied in the CL to the Wolverine soil represented from 0.03% to 0.10% of the N applied in urea and CL.

TABLE 1. Selected Properties and Composition of Clinoptilolite Used in the Study

Property	
CEC, cmol(+) kg ⁻¹	155
Charge density, meq A ⁻²	10.1 ⁻²³
Bulk density, g cm ⁻³	0.76
pH	7.5–8.0
Pore size diameter, angstroms	5
Permeability, m sec ⁻¹	10 ⁻³
Pore volume, % maximum	51
External surface area, m ² g ⁻¹	14–15
Thermal stability, °C	650
Composition	
Na ₂ O, %	4.08
MgO, %	0.44
Al ₂ O ₃ , %	11.5
SiO ₂ , %	68.2
P ₂ O ₅ , %	0.05
K ₂ O, %	3.34
CaO, %	0.4
MnO, %	0.03
Fe ₂ (O ₃), %	1.6
NO ₃ -N, mg kg ⁻¹	2.2
NH ₄ -N, mg kg ⁻¹	6.1

In the mixed treatment, CL and N fertilizer were mixed into the top half of the soil in each column (1.5 kg soil). In the band treatment, CL and N fertilizer were mixed and placed in a band on top of the bottom half of the soil and the remaining half of the soil placed on top (1.5 kg soil). The N application methods mirrored the CL application methods because it would be logical in the field to apply the N with the CL. The total amount of soil in each column was 3 kg. Each treatment combination and the control were replicated four times in a complete randomized design and placed in a climate-controlled growth chamber. The growth chamber was maintained at a temperature of approximately 21°C during the study.

Leachate Analysis

Reverse osmosis water was applied to all columns weekly for 11 weeks for each soil type. For the Portneuf soil, approximately 13 mm of water was applied at Weeks 1 and 2, 53 mm at Week 3, and 26 mm from Weeks 4 to 11. For the Wolverine soil, 26 mm of water was applied each week. The total water applied during the study for both soil types was 286 mm. This depth of water was approximately 33% of the total irrigation water applied to many crops in south-central Idaho during a growing season.

Leachate was collected in 500-mL glass bottles from each column during each water application date for each soil type. The volume of leachate was determined during each leaching event, and a subsample from each column was filtered (45- μm filter) and analyzed for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ using a flow injection analyzer. Masses of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were calculated by multiplying the concentrations by the volumes of leachate collected. The masses were reported on an area basis. The total $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ mass data (summed over all leaching events) are presented in this article for both soils. Including data by leaching event did not add significantly to the conclusions inferred from the data.

TABLE 2. Cumulative Leachate Volume and Mass of NO₃-N, NH₄-N, and Inorganic N (NO₃-N + NH₄-N) in Leachate From CL Rate and Application Method Treatments in Portneuf and Wolverine Soils

Soil	CL Rate Mg ha ⁻¹	Band			Mixed				
		Leachate Volume mL	NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N	Leachate Volume mL	NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N
		kg ha ⁻¹			kg ha ⁻¹				
Portneuf	0	1,371	32.8	0.297	33.1	1,402	11.2	0.338a	11.5
	6.7	1,338	19.2	0.221	19.4	1,225	13.6	0.178b	13.8
	13.4	1,275	25.8	0.362	26.2	1,246	8.8	0.185b	8.9
	20.2	1,319	26.2	0.317	26.5	1,337	12.5	0.121b	12.6
	Mean	1,326	26.0	0.299	26.3	1,303	11.5	0.205	11.7
	ANOVA	0.619	0.691	0.645	0.689	0.225	0.910	0.005	0.912
Wolverine	0	1,498	40.4c	22.0	62.4b	1,498	40.4b	22.0	62.4b
	6.7	1,559	42.2bc	17.5	59.7b	1,559	42.2b	17.5	59.7b
	13.4	1,523	51.8a	17.8	69.7a	1,523	51.8a	17.8	69.7a
	20.2	1,569	50.1a	19.0	69.1a	1,569	50.1a	19.0	69.1a
	26.9	1,519	49.4ab	20.0	69.4a	1,538	50.3a	19.8	70.1a
	Mean	1,534	46.8	19.3	66.1	1,537	47.0	19.2	66.2
ANOVA	0.336	0.024	0.281	0.011	0.373	0.015	0.254	0.006	

Within soils and columns, values with the same letter are not significant at the 0.05 level based on mean separations using the LSD method.

Soil Analysis

After the leaching portion of the study, soils were collected from each column in 5-cm increments from 0 to 25 cm. Soils were air-dried, sieved through a 5-mm screen, extracted with 2 M KCl, and analyzed for NO₃-N and NH₄-N (Mulvaney, 1996) using a flow injection analyzer. Total N was determined by combusting a 100-mg sample using a FlashEA1112 CNH analyzer (CE; Elantech, Lakewood, NJ) (Nelson and Sommers, 1996). Organic N was determined by difference (Total N - Inorganic N). Masses of NO₃-N and NH₄-N for each depth were calculated by multiplying the concentrations by the soil masses. The masses were reported on an area basis. As with the

leachate data, the total NO₃-N and NH₄-N mass data (summed over all soil depths) are presented in this article for both soils because data by depth did not significantly add to the inferred conclusions. Combined data from the soil and leachate will be addressed as the *soil/leachate system*.

Statistical Analysis

Analysis of variance (ANOVA) for the comparison of CL application rate for each soil type and application method was conducted using the Completely Randomized Factorial Model from Statistix 8 (Analytical and Software, 2003). The least significant difference method was used for mean separations.

TABLE 3. Mass of NO₃-N, NH₄-N, Inorganic N (NO₃-N + NH₄-N) in Portneuf and Wolverine Soils at the End of the Study for CL Rate and Application Method Treatments

Soil	CL Rate Mg ha ⁻¹	Band			Mixed		
		NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N	NO ₃ -N	NH ₄ -N	NO ₃ -N + NH ₄ -N
		kg ha ⁻¹			kg ha ⁻¹		
Portneuf	0	54.5	35.6	90.1b	58.3	13.8	72.1
	6.7	85.7	80.3	165.9a	50.0	19.4	69.4
	13.4	74.0	52.1	126.1ab	42.0	35.0	77.0
	20.2	82.3	81.4	163.7a	56.4	15.2	71.6
	Mean	74.1	62.4	136.5	51.7	20.9	72.6
	ANOVA	0.699	0.188	0.044	0.661	0.242	0.378
Wolverine	0	16.6	27.4	44.0	18.2ab	30.3	48.5
	6.7	19.8	40.5	60.3	15.6b	19.5	35.0
	13.4	19.5	44.7	64.2	17.7ab	28.6	46.3
	20.2	16.8	42.2	59.0	20.8ab	23.8	44.6
	26.9	17.6	33.7	51.2	19.7a	27.6	47.2
	Mean	18.0	37.7	55.7	18.4	25.9	44.3
ANOVA	0.121	0.288	0.222	0.040	0.679	0.469	

Within soils and columns, values with the same letter are not significant at the 0.05 level based on mean separations using the LSD method.

Comparison of CL and N application methods for each soil type at each CL application rate was conducted using a Completely Randomized Factorial Model from Statistix 8. Significance was determined at the $\alpha = 0.05$ probability level for all statistical analyses.

RESULTS AND DISCUSSION

Portneuf Soil

Data on the effects of CL application rate for each application method on $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) masses in leachate, soil, and the soil/leachate system are shown in Tables 2, 3 and 4, respectively. For the band and mixed treatments, there were no differences in the leachate volume between the different CL application rates (Table 2). This suggests no effect of CL on water-holding capacity up to an application rate of $20.2 \text{ Mg CL ha}^{-1}$.

Under band application, CL application rate did not affect of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total inorganic N masses in leachate (Table 2). Under mixed application, compared with the control, application of CL decreased $\text{NH}_4\text{-N}$ mass in leachate by 52% (Table 2). However, there were no differences in $\text{NO}_3\text{-N}$ and total inorganic N masses in leachate over CL application rate. The amount of $\text{NH}_4\text{-N}$ in leachate was low compared with $\text{NO}_3\text{-N}$. The ratios of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ masses under band and incorporation application were 87:1 and 56:1, respectively. Ammonium likely was adsorbed onto either soil or CL exchange sites and thus not readily leached. Because of the negative charge location, charge density, and specific open-ring structure, CL is highly selective for NH_4^+ (Ming and Mumpton, 1989). Solution pH may also have affected $\text{NH}_4\text{-N}$ adsorption, as shown by Kithome et al. (1998) who subjected CL to $\text{NH}_4\text{-N}$ and showed that NH_4^+ adsorption on CL increased with increasing pH from 4 to 7. The authors suggested that the formation of new sorption sites and decreased ionic competition caused an increase in $\text{NH}_4\text{-N}$ adsorption.

Under band application of CL, compared with the control, inorganic N mass in the soil was greater (Table 3). Compared

with the control, $20.2 \text{ Mg CL ha}^{-1}$ increased total inorganic N mass in soil by 82% (Table 3). There were no CL application rate differences in $\text{NO}_3\text{-N}$ or $\text{NH}_4\text{-N}$ masses in the soil. Under mixed application, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total inorganic N masses in the soil were the same under all CL application rates (Table 3). The ratios of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ under band and mixed application were 1.2:1 and 2.5:1, respectively. These results support the contention of increased adsorption of $\text{NH}_4\text{-N}$ on to soil or CL exchange sites.

Under both band and mixed application, rate of CL did not influence $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, or inorganic N masses in the soil/leachate system (Table 4). Data suggest that N applied in a band conserved inorganic N in the soil/leachate system more than when mixed. Comparing band and mixed application at each application rate, when CL and N were applied in a band, greater inorganic N mass was in the system compared with when CL and N were mixed into the soil (Fig. 1). Averaged over CL application rates (minus the control), inorganic N mass in the soil/leachate system was 109% greater when N was applied in a band than when mixed. The mass of inorganic N accounted for in the soil/leachate system represented 63% and 32% of the total N applied in fertilizer plus the total initial inorganic N in the soil for the band and mixed treatments, respectively. Differences between the two application methods were possibly caused by a greater rate of NH_4^+ adsorption as previously mentioned or caused by microbial immobilization and denitrification when N was mixed. Protecting $\text{NH}_4\text{-N}$ in the CL matrix could have reduced the effects of nitrifying and denitrifying microorganisms or microorganisms simply using $\text{NH}_4\text{-N}$ as an N source. Although organic N analysis of the soil showed no indication of greater microbial immobilization in this study (data not shown), other studies have shown that urea incorporation into soil increases microbial immobilization compared with band applications (Malhi et al., 1995; Lamond and Moyer, 1983). The relatively small quantity of inorganic N compared with organic N in the soil likely masked any microbial immobilization effects that could be seen with a total N analysis. Additional research will be needed to determine the influence of microbial immobilization as related to results of this study.

TABLE 4. Mass of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, Inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) in Leachate and Soil for Portneuf and Wolverine Soils at the End of the Study for CL Rate and Application Method Treatments

Soil	CL Rate Mg ha ⁻¹	Band			Mixed		
		$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$
----- kg ha ⁻¹ (% of Total N Applied) -----							
Portneuf	0	87.3 (25)	35.9 (10)	123.2 (36)	69.5 (20)	14.1 (4)	83.6 (24)
	6.7	104.9 (31)	80.5 (23)	185.3 (54)	63.6 (19)	19.6 (6)	83.2 (24)
	13.4	99.8 (29)	52.5 (15)	152.3 (44)	50.8 (15)	35.2 (10)	85.9 (25)
	20.2	99.8 (32)	81.7 (24)	190.2 (55)	68.9 (20)	15.3 (4)	84.2 (25)
	Mean	100.1 (29)	62.6 (18)	162.8 (47)	63.2 (18)	21.1 (6)	84.2 (25)
	ANOVA		0.912	0.188	0.109	0.511	0.244
Wolverine	0	55.1 (22)	45.1 (18)	100.2 (40)b	58.6 (24)b	52.3 (21)	110.9 (45)
	6.7	62.5 (25)	65.4 (26)	127.9 (51)a	57.8 (23)b	37.0 (15)	94.8 (38)
	13.4	67.4 (27)	71.8 (29)	139.1 (56)a	69.6 (28)a	46.4 (19)	116.0 (47)
	20.2	65.0 (26)	75.2 (30)	140.2 (56)a	70.9 (28)a	42.8 (17)	113.8 (46)
	26.9	68.5 (28)	64.6 (26)	133.1 (53)a	70.0 (28)a	47.4 (19)	117.4 (47)
	Mean	63.7 (26)	64.4 (26)	128.1 (51)	65.4 (26)	45.2 (18)	110.6 (44)
ANOVA		0.232	0.166	0.024	0.005	0.410	0.093

Within soils and columns, values with the same letter are not significant at the 0.05 level based on mean separations using the LSD method.

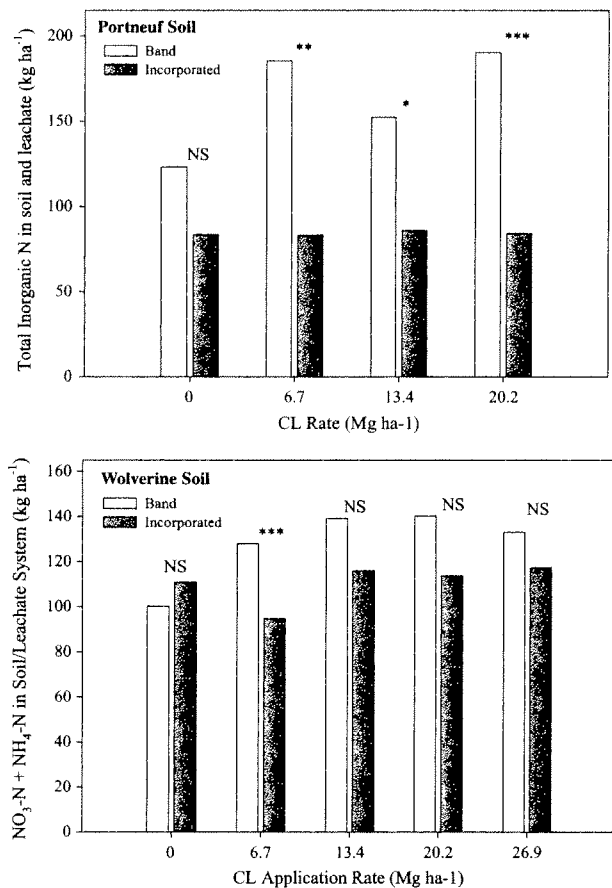


FIG. 1. Total inorganic N in soil/leachate systems of Portneuf and Wolverine soils for band and mixed application methods at each CL application rate. Statistical comparisons are between application methods within CL application rates.

Although microbial immobilization and denitrification were not directly measured, a partial N budget of the soil/leachate system (as shown in Table 4) indirectly lends evidence that denitrification could have influenced differences in $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ masses between application methods. Increased access to and the use of the mixed urea-N by microorganisms and more rapid nitrification were potential reasons for greater microbial immobilization and denitrification (Malhi et al., 1996).

There was likely little loss of urea-N through volatilization as NH_3 in the band or mixed treatments. Research has shown that incorporation of urea into the soil and precipitation or application of irrigation water to broadcast urea shortly after application at rates as low as 5 mm can greatly reduce or eliminate NH_3 volatilization (Malhi et al., 1996; Fenn and Miyamoto, 1981; Harper et al., 1983). In our study, the urease activity was likely low because the soil was air-dried when urea was applied, the urea was thoroughly mixed into the soil, and 13 mm of water was applied shortly after urea application.

Wolverine Soil

Data on the effects of CL application rate on $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total inorganic N masses in leachate, soil, and the total soil/leachate system are shown in Tables 2, 3, and 4, respectively. Similar to the Portneuf soil, there were no differences in the leachate volume between the different CL application

rates (Table 2). This suggests that there was no effect of CL on water-holding capacity in this soil up to an application rate of $26.9 \text{ Mg CL ha}^{-1}$.

Under both band and mixed application, compared with the control and the lowest CL application rate, applying CL at rates of 13.4 to 26.9 Mg ha^{-1} increased $\text{NO}_3\text{-N}$ and total inorganic N leachate masses (Table 2). Rate of CL did not influence $\text{NH}_4\text{-N}$ leachate mass losses. Under band and mixed application, compared with the control and the lowest CL application rate, application of CL at rates of 13.4 to 26.9 Mg ha^{-1} increased total inorganic N leachate masses by 14% (Table 2). Similar to the Portneuf leachate data, the amount of $\text{NH}_4\text{-N}$ in leachate was low compared with $\text{NO}_3\text{-N}$. The same explanation given for this difference with the Portneuf soil applies to the Wolverine soil.

Under both band and mixed applications, CL application rate did not affect $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total inorganic N masses in the soil (Table 3). The ratios of $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ under band and incorporation application were 0.48:1 and 0.71:1, respectively. These results support the contention of increased adsorption of $\text{NH}_4\text{-N}$ on to soil or CL exchange sites.

Under band application, compared with the control, application of CL increased the total inorganic N mass in the soil/leachate system by 35% (Table 4). There was not an influence of CL rate on $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ masses in the soil/leachate system. Under incorporation application, compared with the control and the lowest CL application rate, applying CL at rates of 13.4 to 26.9 Mg ha^{-1} increased $\text{NO}_3\text{-N}$ soil/leachate system mass by 21% (Table 4). There was not an influence of CL rate on $\text{NH}_4\text{-N}$ and inorganic N masses in the soil/leachate system. Data suggest that N applied in a band may conserve total inorganic N in the soil/leachate system more than when N was mixed. The evidence is not as clear as with the Portneuf soil, but there is a consistent trend for greater total inorganic N in the soil/leachate system when CL is band applied than when mixed (Fig. 1). The total inorganic N mass accounted for in the soil/leachate system represented 54% and 47% of the total N applied in fertilizer plus the total initial inorganic N in the soil for the band and mixed treatments, respectively.

CONCLUSIONS

Applying CL influenced inorganic N in both soils, likely caused by NH_4^+ adsorption on to soil and CL exchange sites as well as being protected within CL pores from microorganism assimilation. In the Portneuf soil, applying N fertilizer in a band conserved available soil inorganic N in the soil/leachate system compared with when it was mixed. When N fertilizer was mixed, a greater rate of microbial immobilization, nitrification, and denitrification potentially resulted compared with when the N fertilizer was banded. In the Wolverine soil, it is less clear what the effect of application method was on available inorganic N in the soil/leachate system, although there was a trend for greater inorganic N conservation under band application. In these soils, application of CL at rates as low as 6.7 to 13.4 Mg ha^{-1} can help conserve available inorganic N. Based on the results, we suggest evaluating the use of CL in the field on a range of different textures to increase the amount of available inorganic N conserved in the soil system.

ACKNOWLEDGMENTS

This study was supported by Zeocorp LLC, CRADA no. 58-3k95-8-1283. Mention of a specific product or vendor does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or imply its approval to the exclusion of other products that may be suitable.

REFERENCES

- Analytical and Software. 2003. Statistix 8. Analytical and Software, Tallahassee, FL.
- Bouwmeester, R. J. B., P. L. G. Vlek, and J. M. Stumpe. 1985. Effect of environmental factors on ammonia volatilization from a urea-fertilized soil. *Soil Sci. Soc. Am. J.* 49:376–381.
- Fenn, L. B., and S. Miyamoto. 1981. Ammonia loss and associated reactions of urea in calcareous soils. *Soil Sci. Soc. Am. J.* 45:537–540.
- Harper, L. A., V. R. Catchpoole, R. Davis, and K. L. Weir. 1983. Ammonia volatilization: Soil, plant and microclimate effects on diurnal and seasonal fluctuations. *Agric. J.* 75:2112–2218.
- Huang, Z. T., and A. M. Petrovic. 1994. Clinoptilolite zeolite influence on nitrate leaching and nitrogen use efficiency in simulated sand based golf greens. *J. Environ. Qual.* 23:1190–1194.
- Kithome, M., J. W. Paul, L. M. Lavkulich, and A. A. Bomke. 1998. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. *Soil Sci. Soc. Am. J.* 62:622–629.
- Lamond, R. E., and J. L. Moyer. 1983. Effects of knifed vs. broadcast fertilizer placement on yield and nutrient uptake by tall fescue. *Soil Sci. Soc. Am. J.* 47:146–149.
- MacKown, C. T., and T. C. Tucker. 1985. Ammonium nitrogen movement in a coarse-textured soil amended with zeolite. *Soil Sci. Soc. Am. J.* 49:235–238.
- Malhi, S. S., M. Nyborg, and J. T. Harapiak. 1995. Recovery of ^{15}N -labeled fertilizers applied to bromegrass on a Thin Black Chernozem Soil. *Can. J. Soil Sci.* 75:539–542.
- Malhi, S. S., M. Nyborg, and E. D. Solberg. 1996. Influence of source, method of placement and simulated rainfall on the recovery of ^{15}N -labelled fertilizers under zero tillage. *Can. J. Soil Sci.* 76:93–100.
- Minato, H. 1968. Characteristics and uses of natural zeolites. *Koatsu Gasu.* 5:536–547.
- Ming, D. W., and F. A. Mumpton. 1989. Zeolite in soils. *In: Minerals in Soil Environments.* J. B. Dixon and S. B. Week (eds.). SSSA Publisher Inc, Madison, WI, pp. 874–911.
- Moore, F. D., M. D. Lewis, and K. L. Goldsberry. 1982. Greenhouse experiments with ammonium exchanged clinoptilolite and urea/cclinoptilolite mixtures. *In: Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture.* W. G. Pond and F. A. Mumpton (eds.). Westview Press, Boulder, CO.
- Mulvaney, R. L. 1996. Nitrogen—Inorganic forms. *In: Methods of Soil Analysis, Part 3—Chemical Methods.* D. L. Sparks (ed.). SSSA, Madison, WI, pp. 1123–1184.
- Nelson, D. W., and L. E. Sommers. 1996. Total carbon, organic carbon, and organic matter. *In: Methods of Soil Analysis, Part 3—Chemical Methods.* D. L. Sparks (ed.). SSSA, Madison, WI, pp. 975–977.
- NRCS, 2009a. Soil Extent Mapping Tool, USDA-NRCS, Washington, DC [Online]. Available from: <http://www.cei.psu.edu/soiltool/semtool.html> (verified March 13, 2009).
- NRCS, 2009b. Web Soil Survey, USDA-NRCS, Washington, DC [Online]. Available from: <http://websoilsurvey.nrcs.usda.gov/app/HomePage.htm> (verified March 13, 2009).
- Perrin, T. S., J. L. Boettinger, D. T. Drost, and J. M. Norton. 1998. Decreasing nitrogen leaching from a sandy soil with ammonium-loaded clinoptilolite. *J. Environ. Qual.* 27:656–663.
- Prasertsak, P., J. R. Freney, O. T. Denmead, P. G. Saffigna, B. G. Prove, and J. R. Reghenzani. 2002. Effect of fertilizer placement on nitrogen loss from sugarcane in tropical Queensland. *Nutr. Cycl. Agroecosyst.* 62:229–239.
- Stoilov, G., and N. Popov. 1982. Agricultural uses of natural zeolites in Bulgaria. *In: Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture.* W. G. Pond and F. A. Mumpton (eds.). Westview Press, Boulder, CO.
- Tisdale, S. L., W. L. Nelson, J. D. Beaton, J. L. Havlin. 1993. *Soil Fertility and fertilizers.* 5th edition. MacMillan Publishing Company, New York, NY.
- Torri, K. 1978. Utilization of natural zeolites in Japan. *In: Natural Zeolites: Occurrence, Properties, Use.* L. B. Sand and F. A. Mumpton (eds.). Pergamon Press, Elmsford, NY, pp. 441–450.
- Tsitsishvili, G. V., T. G. Andronikashvili, G. N. Kirov, and L. D. Filizova. 1992. *Natural Zeolites.* Ellis Horwood, New York, NY.
- US EPA, 2006. National Water Quality Inventory: 1994 Report to Congress. Available from: <http://www.epa.gov/owow/305b/94report/> (verified February 9, 2009).
- Vaughan, D. E. W. 1978. Properties of natural zeolites. *In: Natural Zeolites: Occurrence, Properties, Use.* L. B. Sand, and F. A. Mumpton (eds.). Pergamon Press, Elmsford, NY, pp. 353–372.
- Williams, P. H., R. J. Tregurtha, and G. S. Francis. 2003. Fate of urea applied to winter spinach in New Zealand. *Nutr. Cycl. Agroecosyst.* 67:245–254.